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PHOTOCHEMICAL STUDIES OF SECONDARY NITRAMINES. PART II. ULTRAVIOLET PHOTOLYSIS AND OZONOLYSIS OF RDX IN AQUEOUS SOLUTIONS

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The purpose of this study was to determine the feasibility of chemical degradation of RDX by ultraviolet-ozone process which had been previously developed for eliminating TNT from pink water. A study of UV photolysis at 254, 300 and 350 nm wavelengths, ozonolysis alone and a combination of O_3 and UV (350 nm) on aqueous solutions of RDX was undertaken. The results indicate that O_3 + UV in combination efficiently degrade RDX to gaseous products. These products are further compared with those obtained by photolysis and thermal decomposition of samples of crystalline RDX.

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FOREWORD

This report details the work accomplished under the technical sponsorship (OCMS #4932.05.4114.0) of the Modernization and Special Technology Branch of the Manufacturing Technology Division, Large Caliber Weapons Systems Laboratory, ARRADCOM, Dover, NJ.

The report includes work on UV/Ozone process for chemical degradation of RDX as a part of the broader "pink water" pollution abatement problem at the Army ammunition loading and packaging plants.

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INTRODUCTION

Since 1970 increased emphasis has been placed on eliminating pollution arising from munitions manufacturing and processing plants. One serious pollution problem is the removal of the nitro bodies from the so-called pink water which is the wash water from loading, assembling and packaging operations involving TNT. This water dissolves up to 150 ppm of TNT, about 80 ppm RDX and much smaller amounts of other nitro compounds. On exposure to sunlight, the photochemical reactions of TNT generate several colored species which impart the characteristic pink color to the water. Under a contract from the Volunteer Army Ammunition Plant (VAAP), Chatanooga, Tenn, IIT Research Institute (IITRI) studied ozonolysis (Ref 1) as a means to destroy the nitro compounds and showed that pink water at its normal pH of 5.6 was rendered colorless and more acidic (pH = 4-5) on treatment with ozone (O_3). However, neutralization to pH 7 returned new colored species which were presumed different from those formed photochemically. If the ozonolysis was carried out at an alkaline pH ($\sim$ 8 to 10.5) the color could be removed permanently but this process was inefficient in the use of ozone.

The IITRI project then experimented (Ref 2) with an ozone plus ultraviolet irradiation process to decontaminate the pink water, this combination process having been found previously (Ref 3) to be effective in oxidation of refractory organic materials in municipal waste waters. For these experiments synthetic pink water, made by dissolving TNT (160 ppm) in water, was used and the efficiency of the process was measured by the determination of the total organic carbon (TOC) as a function of O_3 + UV dosage. A germicidal lamp was used in these experiments as the source of ultraviolet light. A dramatic UV effect was observed, relative to the use of O_3 alone, and the initial total organic carbon levels of about 60 mg/l dropped to 17 mg/l in two hours. In addition, it was found that more than 85% of the lost organic carbon appeared as CO_2, thus obviating the problem of secondary pollution from intermediate degradation products of TNT. The chemistry and engineering aspects of the UV + O_3 process were further investigated in the feasibility studies conducted by Westgate Research Corporation (Ref 4) and Walden Research Division (Ref 5). While further details of the above studies of the O_3-UV process will not be included here, it is important to emphasize that this process was demonstrated to be effective in degrading the TNT and related nitro-aromatic compounds in pink water to innocuous end products. RDX, which is a common constituent of pink water (80 ppm) was not included in the above studies and the reactions of RDX under O_3 + UV oxidative treatment have not been investigated. Since it would be desirable to have a method common to both TNT and RDX, a study of the latter was initiated in this laboratory and the results are reported here.

The general approach for this RDX study consisted of an investigation of its gross photochemical degradation in aqueous solutions and, independently, its oxidative degradation by ozone. In each case, a determination of the products of degradation was attempted together with the time element for each process. It was hoped that this approach would lead to a better understanding of the chemistry involved. The combined effect of O_3-UV was then studied. During this work a report (Ref 6) appeared in the literature describing the photolysis of tap water-dissolved RDX under laminar flow conditions. One other report of a brief study of RDX photolysis dealt with photolysis in organic solvents (Ref 7).

EXPERIMENTAL AND RESULTS

Solution of RDX

A saturated (50 mg/l) stock solution of pure RDX (> 99.8%) in distilled water was prepared. This solution was used, after appropriate dilution, for all the experiments except the irradiations of polycrystalline RDX. Absorption spectra were always measured after the solutions were diluted to give optimum absorption.

Photolysis of Aqueous Solutions of RDX at 254 nm

In the first set of experiments to photolyze RDX, a Rayonet photochemical reactor (Ref 8), Model RPR-100, consisting of a circular array of 16 low pressure Hg lamps (254 nm) with a total output of 35 watts was used. It was however, found that in this reactor even saturated solutions of RDX (approximately 50 mg/l) were fully depleted of RDX in 10 minutes (Fig 1). The subsequent experiments were carried out with a very low intensity spectroline quartz pencil lamp (UV) placed 4" from a 1 cm Beckmann quartz spectrophotometer cell containing the RDX solution. Figure 2 shows the disappearance of RDX absorption with increasing time of UV-irradiation. Under these conditions the degradation of RDX appears to be complete in less than one hour. Exact correlations of the UV energy with RDX disappearance were not attempted.

Analysis of RDX

Two methods, to be called A&B, were employed for the analysis of RDX remaining in the solutions. In method A the concentration was obtained directly from a calibration plot of concentration versus optical density (O.D.). In method B, illustrated in Figure 3 (curves 3 & 5) the absorbance of the experimental solution was measured at all times against the standard strating solution to compensate the overlapping absorption edge near the λ_{max} of RDX. At the same time solvent and solution compartments of the spectrophotometer were interchanged for convenience in the recorded output. Thus while curves 1 and 2 in Figure 3 represent normal absorption of RDX solution before and after 30 minutes photolysis, respectively, curve 3 was obtained by the compensation method and its peak height is a direct measure of RDX consumed in the photolysis.

Relative Photolysis Rates at 254, 300 and 350 nm

The photolysis experiments were also extended to long wave UV (300,350 nm) radiation to more nearly simulate solar radiation. A comparative study of three wavelengths was accomplished using a Rayonet reactor with four lamps each of RPR-2537, RPR-3000 and RPR-3500 type with rated outputs of 9, 5 and 24 watts, respectively. Aqueous solutions of RDX at a concentration of 20 mg/l were irradiated in spectrophotometer cells placed at the center of the reactor. The results of this series of runs are summarized in Figure 4, curves 1 to 3.

Ozonolysis of Aqueous Solutions of RDX

A Welsbach, Model T-816 ozonizer (Ref 9) was used as the source of ozone. The ozone was generated by the passage of an electric discharge (70 volts, 68 watts) through oxygen flowing at a rate of 500 ml/min. Under these conditions, the ozone concentration in the exit flow was 45 mg/min as determined by iodometric analysis (Ref 9). The ozonolysis was typically conducted by bubbling the O_2-O_3 mixture through a gas wash bottle containing 250 ml of RDX solution at a concentration of 20 mg/l. Five ml portions taken at different times were analyzed for RDX content by UV spectrophotometry. The data from one such run are included in Figure 4, curve 4.

Concurrent Photolysis and Ozonolysis

For these experiments the 350 nm UV source which caused the lowest photolysis rate was used in conjunction with a O_3 + O_2 flow rate of 0.5 l/min (45 mg O_3/min). The concentration of the RDX solution was 20 mg/l and, as the reaction progressed, the optical density of the solution at 238 nm was measured versus time. Table 1 summarizes these results and shows the relative rates of photolysis, ozonolysis and the combined application of both UV and O_3. The numbers represent the progressive decrease in the optical density at 238 nm (λ_{max} of RDX).

Table 1

Ozonolysis, photolysis and their combined application for the chemical degradation of RDX

Reaction time, hrs	Changes in optical density		
	Ozonolysis	Photolysis	Ozonolysis & photolysis
0	0	0	0
1	0.12	0.07	0.64
2	0.19	0.19	0.91
3	0.22	0.30	0.93
4	0.29	0.37	0.94
5	0.33	0.41	0.94
6	0.36	0.52	
7	0.38	0.57	
8	0.43	0.60	
9	0.46	0.64	
10	0.49	0.56	
11	0.52	0.66	
12		0.67	
13		0.70	
14		0.75	
15		0.75	

Analysis of Gaseous Products

Since UV-absorption spectroscopy indicated a drastic degradation of RDX molecule at 254 nm without giving rise to new absorption in the UV or visible region, it was decided to analyze the photolysis solution for gaseous products. A special cell was designed in which the solution could be outgassed, irradiated with UV and then outgassed a second time to collect the low molecular weight gaseous products. The gaseous products were analyzed using a DuPont 21-492 mass spectrometer. The significant portions of the mass spectrum in two runs, corrected for background are shown in Table 2.

Table 2

Mass spectra of the gaseous products of photolysis of RDX

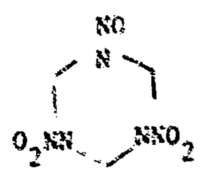
m/e*	Run 1 Relative abundance	Run 2 Relative abundance
22	-	-
28	1230	960
29	32	50
30	840	785
31	40	14
44	1410	1300
45	20	19

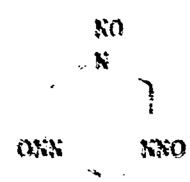
These mass spectra indicate the principal products to be N_2O (m/e 44, 30), NO (m/e 30) and N_2/CO (m/e 28) with trace amounts of formaldehyde (m/e 30,29).

* Mass-to-charge ratio

GC/MS Analysis

Previous studies of thermal decomposition (Ref 10,11) of RDX identified as gaseous products N_2O, CH_2O, N_2, CO, CO_2, HCN and H_2O with a polymeric residue (~ 1%).[2] One report (Ref 7)[2] indicated the presence of trace amounts of two solid products, 1-nitroso-3,5-dinitro-1,3,5-triaza cyclohexane (I) and 1,3,5-trinitroso-1,3,5-triazacyclohexane (II). In the hope of detecting the same or closely related products under UV + O_3 degradation, GC and GC/MS analyses were attemped. Photolyzed aqueous solutions of RDX, as well as those subjected to both





O_3 and UV, were concentrated and analyzed by GC using a SE-30 column. The observed peaks, when admitted to a mass spectrometer, gave evidence of only low molecular weight (< m/e 44) species (Table 3). One sample partially decomposed by UV + O_3 was extracted with ethylene dichloride and the latter solution was concentrated and analyzed directly by mass spectrometry. The only species found in this sample was unreacted RDX with no evidence of impurities above the background level.

Table 3

GC/MS Analysis of photolyzed RDX solutions

Fragments m/e	Relative abundance, chart divisions		
	GC peak [illegible]	GC peak #2	GC peak #3
28	1300	100	100
29	850	250	50
30	2100	800	170
42			30
44	2900	1000	190
54		60	100
74			130
81		90	130

Photolysis of Polycrystalline RDX

Several irradiations of polycrystalline samples of RDX were attempted in which the product analysis was expected to be more manageable. The irradiations were carried out in a quartz spectrometer cell (1 mm x 1 cm x 5 cm) attached to a vacuum manifold through a ground joint. The vacuum manifold was connected to the inlet system of the mass spectrometer (duPont 21-492). In each experiment 200 mg of RDX were placed in the cell and the latter evacuated. One sample was irradiated with 254 nm UV light (low pressure Hg lamp fitted with appropriate filters). The gas liberated by photolysis was analyzed by bleeding samples into the mass spectrometer at intervals of time up to 3 1/2 hours. The constituents of the gas were determined from the known cracking patterns and initial calibrations. Tables 4 and 5 show the detailed analysis.

Table 4

Photolysis products of RDX at λ = 254 nm (ccmm)

	Time (minutes)						
	30	60	90	120	150	180	210
N_2	22.0	35.0	46.0	54.0	60.0	65.0	70
NO	18.0	27.8	34.0	39.0	42.0	46.0	49
N_2O	4.6	7.8	10.4	12.8	14.1	15.5	17.1
CO	3.9	8.8	11.1	14.1	18.0	19.5	20.5
CO_2	2.4	5.5	8.1	9.8	11.5	13.6	15.2
HCN	0.5	0.9	1.2	1.4	1.6	1.7	1.9
HCHO	1.3	2.6	3.1	3.2	3.3	3.3	3.4
H_2O	0.2	0.3	0.5	0.6	0.8	1.1	1.5
H_2	0.3	0.4	0.5	0.5	0.6	0.7	0.7

Table 5

Photolysis products of RDX at λ = 310-330 nm (ccmm)

	Time (minutes)						
	30	60	90	120	150	180	210
N_2	10.0	30.5	53	72.1	9.12	107	121
NO	3.6	9.5	16.0	23.0	31.0	38	47
N_2O	2.6	8.1	13.6	19.3	24.5	28.4	33.3
CO	0.8	3.4	5.9	7.8	10.2	11.8	14.2
CO_2	1.6	4.3	7.2	10.0	12.9	15.0	17.4
H_2O	0.1	0.5	1.0	1.5	2.2	2.9	3.9
H_2	-	-	0.1	0.1	0.1	0.1	0.1

RESULTS AND DISCUSSION

Photolysis of RDX in Solution

The absorption spectra of RDX and other nitramines, as well as the photolysis of dimethylnitramine, were the subjects of earlier publications (Ref 12, 13) from this Division. Aqueous solutions of RDX showed a broad absorption extending to 300 nm in the UV with a λ_{max} at 238 nm and an extinction of 11,000. It was decided, therefore, to use UV sources in this wavelength range for the irradiation, e.g., 254, 300 and 350 nm. Since the earlier study of dimethylnitramine (DMNA) showed that a major photolytic product was the corresponding nitrosamine which absorbed in the UV at 235 and 370 nm, a preliminary experiment was run with RDX to determine whether a similar process occurred. There was no evidence of such species and it was possible to use the absorbence of RDX for analytical purposes.

Figures 1 and 2 clearly demonstrate the rapid degradation of RDX in aqueous solutions under the influence of 254 nm UV radiation. Indeed, with the use of as little as 35 watts output in these experiments most of the RDX was destroyed in about 10 minutes. This is seen more strikingly in Figure 3, curve 3 obtained by the method B of analysis.

The relative efficiencies of different wavelengths of UV light can readily be seen in Figure 4. It is apparent that the 350 nm radiation, even with 3 times the intensity of the 254 nm source, was much less effective in degrading RDX. This is understandable since the absorption edge for RDX lies in this wavelength range. It was found independently that solid RDX was very stable to 366 nm UV and evolved no gas in over 10 hours.

Ozonolysis

This study consisted of conducting photolysis and ozonolysis under identical conditions and then comparing these experiments with the combined reaction in order to determine the possible enhancement of the rate of degradation. It can be seen in Figure 4 that O_3 at a relatively high concentration was much slower in degradation of RDX when used alone. From curve 4 one can estimate that about 27 g. O_3 passed through the solution containing 5 mg RDX and yet, only $\sim$ 50% of the RDX was consumed. This inefficiency was probably due to excessively high flow rate of O_3 which allowed little contact time with RDX.

Interestingly, an unmistakable synergistic effect was observed when O_3 and 350 nm UV were used together. It can be seen in Table 1 that each of the two reagents destroys approximately half of the

RDX in the solution in ∿ 10 hours, but when used in combination, ∿ 95% of the RDX was degraded in 5 hours. There has been some speculation about the role of singlet oxygen in this reaction (Ref 4) but the present work could not shed any light on this speculation.

Degradation Products of RDX

Curve 6 in Figure 2 shows that most of the degradation products of RDX were volatile because they could be driven out by sparging with N_2. These spectra (Fig 2) also indicate that condensible products (I) and (II), the spectra of which are shown in Figure 5, were not formed in these experiments. Typical compositions of the gaseous products are shown in Tables 2 and 3. As indicated in the experimental section, they consist of low molecular weight species, the largest being N_2O. However, these analyses are not strictly quantitative.

Photolysis of Pure RDX

The aqueous solution of RDX used for this study was very dilute due to the low solubility of RDX in water. This, combined with the fact that RDX essentially degrades to gaseous products presented severe analytical problems. To avoid these problems, experiments were designed in which polycrystalline samples of RDX were directly photolyzed and the products determined quantitatively. It was possible by this means to establish the general nature of the chemical degradation products. Typical analyses are shown in Tables 4 and 5 and these products appear to be similar to those which gave rise to the mass spectral fragments shown in Tables 2 and 3.

Thermal Decomposition of RDX

It is noteworthy that the thermal decomposition products of RDX also bear a resemblance to those obtained in the photolysis and/or ozonolysis. Table 6 summarizes the thermal decomposition products found in an earlier study (Ref 7).

Table 6

Moles of product/mole of RDX normalized to 100% decomposition

% RDX decomposed	CO_2	N_2O	N_2	NO	CO	HCN	CH_2O	H_2O
19	.54	1.22	1.08	.23	.41	.23	--	--
30	.66	1.47	1.04	.49	.54	.23	--	1.67
69	.62	1.25	1.16	.49	.56	.16	.72	1.10
78	.50	1.26	.83	.44	.48	.09	--	--
93	.61	1.36	.99	.45	.52	.03	.97	.97

It is evident that in the photodegradation of RDX, in both aqueous solution and in the solid state, much smaller amounts of formaldehyde were formed than in the thermal decomposition. This may be an experimental artifact in that the HCHO produced in thermal decomposition runs could diffuse away from the heated region of the apparatus while in photolysis it could undergo secondary photoreactions. Also, HCN was not observed in the present experiments in aqueous solution, whereas it was clearly detectable in the other experiments. Unfortunately, the analysis of products described in this report are not sufficiently quantitative to give exact yields. The limited scope of this work did not permit designing the large scale experiments needed for quantitative determinations. In view of the complexity of such experiments, it would be desirable to combine them with the UV + O_3 process for TNT. Past work on TNT (Ref 1) showed that most products are gaseous and experiments with TNT and RDX together would have the advantage of revealing secondary reactions among the products from the two compounds. Thus, while undesirable products like HCHO, N_2O, CO and HCN may be formed in these reactions, their relative importance can not be judged precisely until actual "pink water" samples are subjected to the UV + O_3 treatment.

CONCLUSIONS

The work reported here establishes that: (1) aqueous RDX solutions undergo rapid photochemical degradation with 254 nm UV light leading to low molecular weight gaseous products (2) ozone degrades RDX much less efficiently than UV (3) the combined use of O_3 and UV exhibits a marked synergistic effect in that the combined degradation rate is greater than the sum of the two individual degradation rates (4) photolysis at two wavelengths and thermal decomposition of crystalline RDX give products generally similar to those of the photolysis in solution, and finally (5) the appearance of HCHO and HCN is subject to variation, possibly due to secondary reactions. Condensible products do not seem to be formed in the reactions studied. A quantitative determination of gaseous products can only be attempted in large scale experiments. It thus appears that the O_3 and UV process in pink water will be effective in destroying both RDX and TNT.

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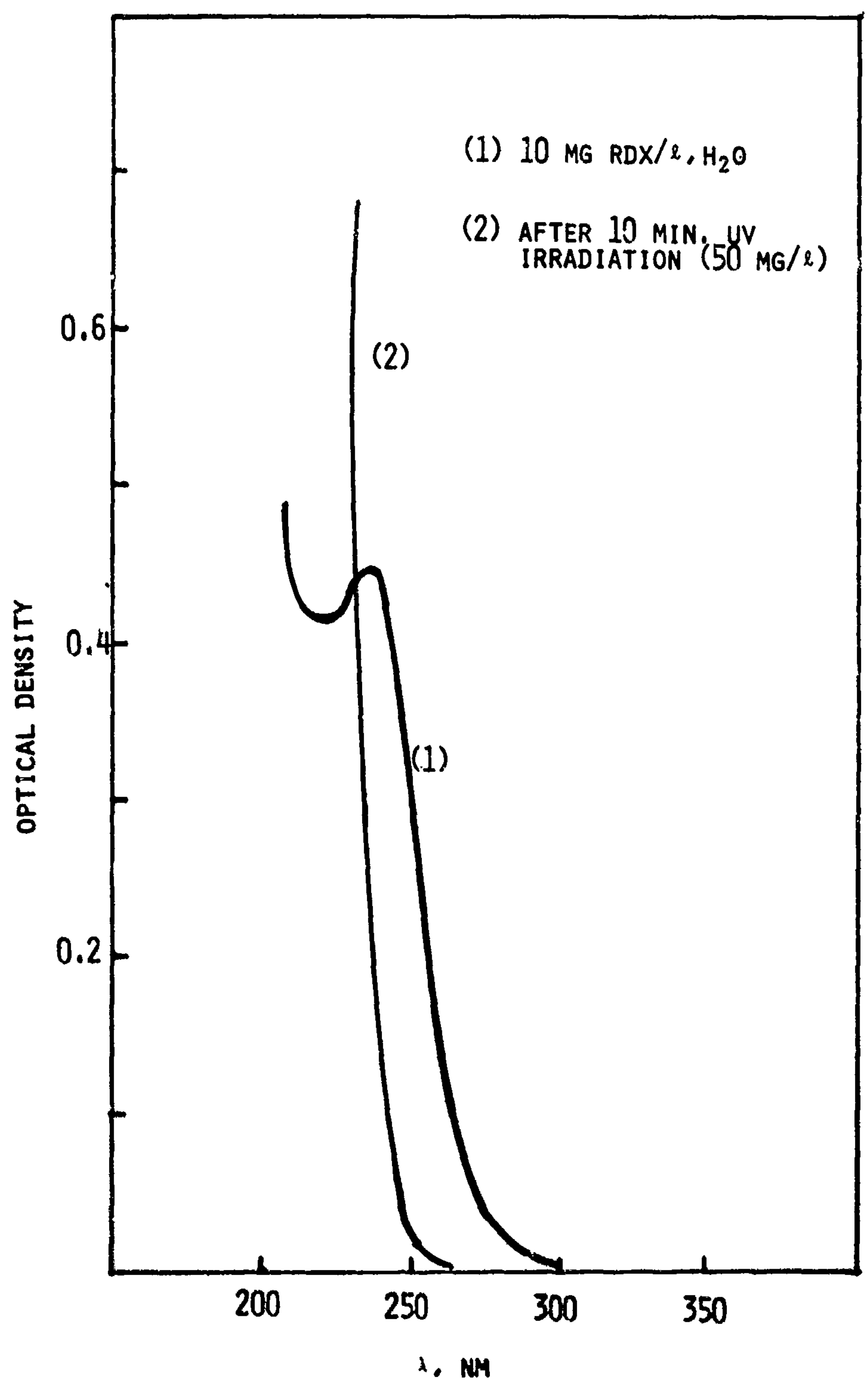

Fig 1 UV spectra of RDX before and after photolysis

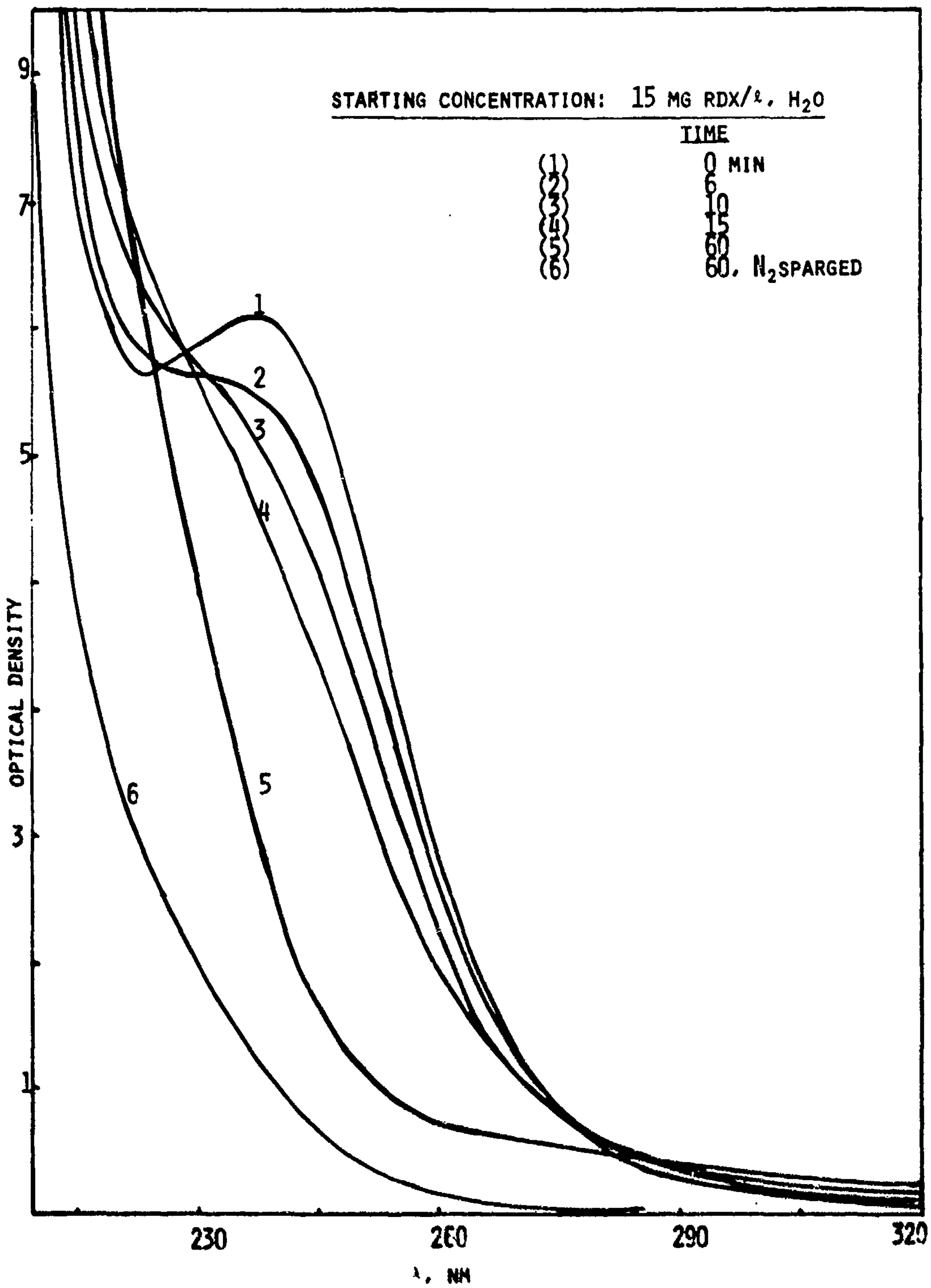

Fig 2 Absorption spectra of RDX solutions with photolysis

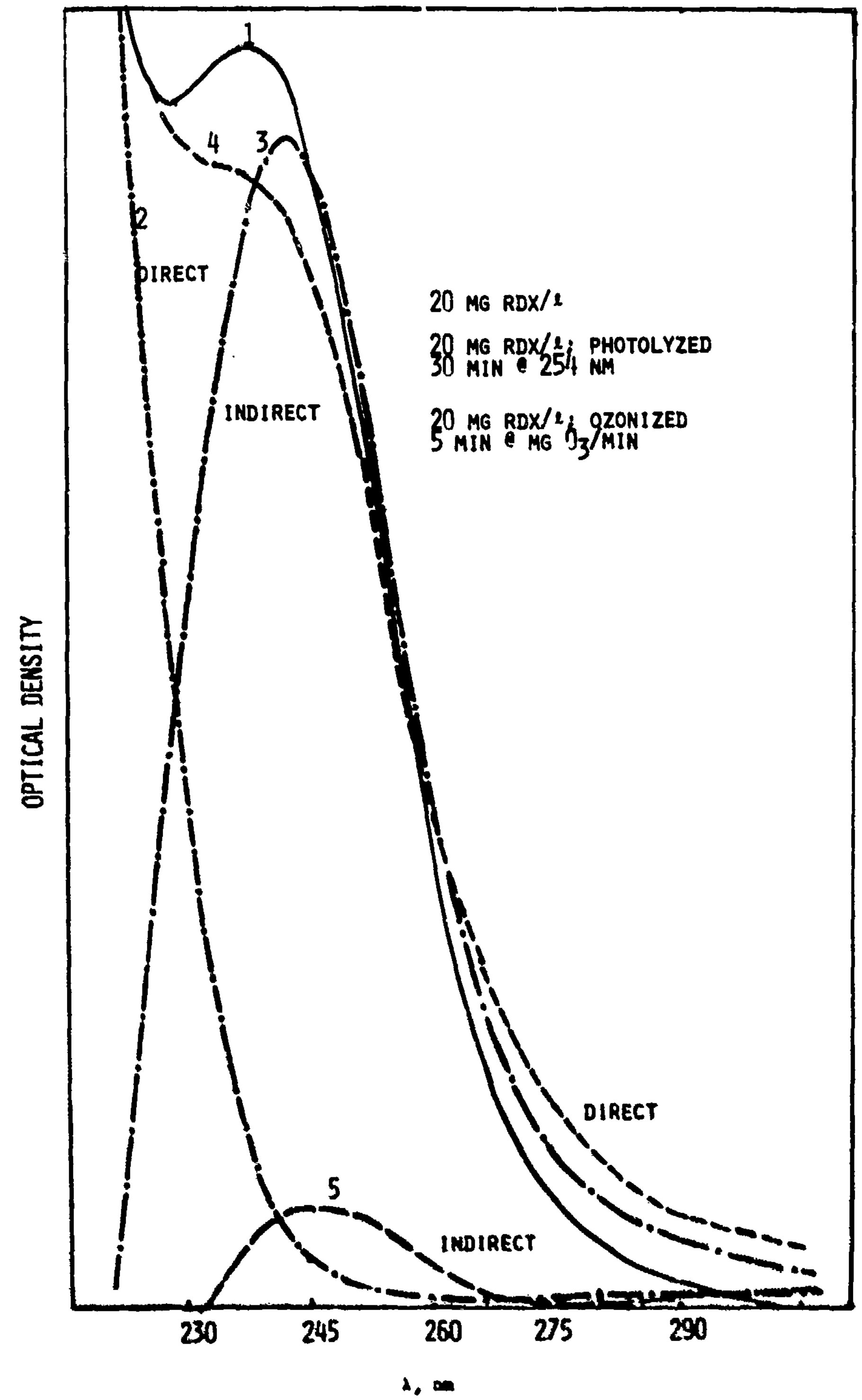

Fig 3 Spectra of aqueous RDX solutions by the direct and indirect methods

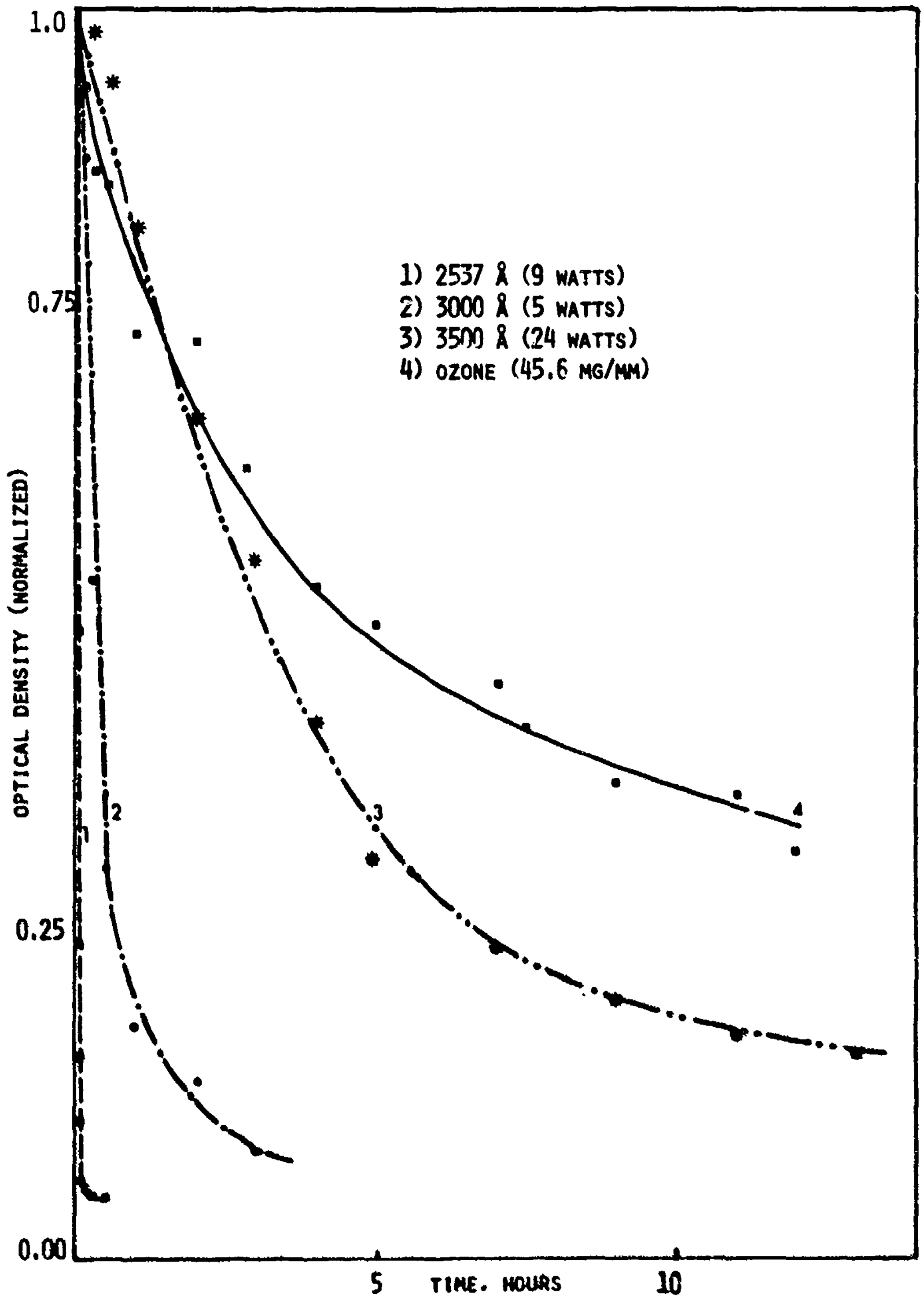

Fig 4 Change in absorbance of aqueous RDX solutions with photolysis/ozonolysis time

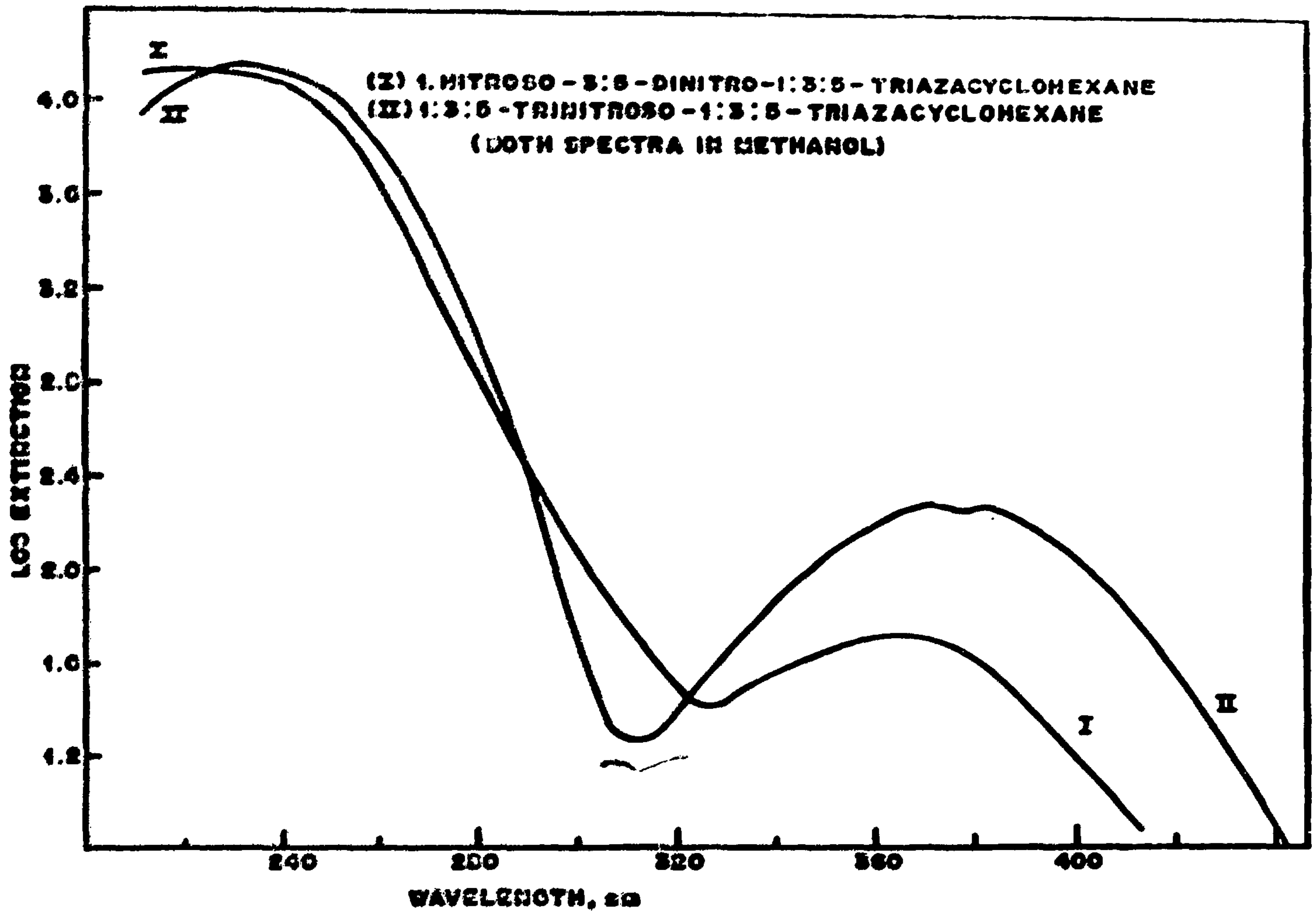

Fig. 5 Spectra of (I) 1-nitroso - 3:5-dinitro-1:3:5-triazacyclohexane and of (II) 1:3:5-trinitroso-1:3:5-triazacyclohexane, both in methanol

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